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(54) ELEMENT DE COMPOSITION POUR LAVE-VAISSELLE

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(54) DISHWASHING COMPOSITION PORTION

(S7) 2322 The Invention relates to a low water content-focanting composition, portion, in particular additionation or more front composition, compating one more front compating or more front compating at least one water material and at least one active washing-formulation partly or fully surrounded by said at least-one water-activities power material. 2



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(54) ELEMENT DE COMPOSITION POUR LAVE-VAISSELLE

(54) DISHWASHING COMPOSITION PORTION

(57) The invention relates to a low water content cleaning composition portion, in particular a dishwashing composition, comprising one or more enclosures comprising at least one water-soluble polymer material and at least one active washing formulation partly or fully surrounded by said at least one water-soluble polymer material.

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Abstract

"Dishwashing composition portion"

The invention relates to a low water content cleaning composition portion, in particular a dishwashing composition, comprising one or more enclosures comprising at least one water-soluble polymer material and at least one active washing formulation partly or fully surrounded by said at least one water-soluble polymer material.

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Dishwashing composition portion

Field of the Invention

The present invention relates to a dishwashing composition portion having an enclosure comprising a water-soluble polymer material and at least one active washing formulation.

Background of the Invention

Cleaning compositions in single-dose amounts are known from the prior art. For instance, earlier patent application DE 198 31 703 discloses a portioned cleaning composition formulation in a water-soluble film pouch for use in washing machines or dishwashers, at least 70% by weight of the particles of the formulation having sizes of >800 µm. In addition, earlier patent application DE 199 09 271 describes the production of multiphase cleaning composition tablets for use in machine laundering or washing, the size of the tablets in respect of the active substance content being such that the active washing formulations are sufficient for exactly one wash cycle in the machine.

Dishwashing compositions for use when washing in a washbasin or washing-up bowl have been provided in the prior art in liquid form, generally packaged in containers or bottles provided with closable spouts or dosing apertures. An advantage of such packaging forms that the user could dose the dishwashing composition freely, adding more if desired or felt necessary. A disadvantage of such packaging forms, however, was that precise dosing of the dishwashing composition required a certain degree of experience, and the composition was frequently underdosed or overdosed. Underdosing generally necessitated the addition of further dishwashing composition during the 35 wash, which again entailed the risk of overdosing, while overdosing itself was and is generally undesirable on environmental and economic grounds. A further disadvantage was that there were often residues of dishwashing composition in the spouts or dosing apertures, which either ran down the outside of the

bottles or containers and left unwanted residues on the bottles or containers, or on the surfaces on which they were placed, or which blocked the spouts or dosing apertures.

A further disadvantage of the dishwashing compositions provided in the conventional pack forms was that these compositions, according to the wishes of the consumers, had to be homogeneous - in particular, they had to be clear. This requirement, dictated by custom, had the consequence that it was not possible to incorporate into such compositions components which were not uniformly distributed in the fully formulated dishwashing composition or which settled in the course of storage or during the time that the opened bottle or container was left standing.

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A further problem of conventional dishwashing compositions was the impossibility of incorporating components whose stability during storage is impaired by other components of the dishwashing composition. This was the reason, for example, why the dishwashing compositions could not be formulated with enzymes effective during the wash, especially not in hand dishwashing compositions, since, in the aqueous medium of customary dishwashing compositions, problems occurred with the stability of the enzymes.

Summary of the Invention

It was therefore an object of the invention to overcome the aforementioned disadvantages of the prior art. A particular object of the invention was to provide dishwashing compositions in portions ready for use for one wash. A further object of the invention was to provide dishwashing compositions which can include components which cannot normally be distributed homogeneously in hand dishwashing compositions without precipitating, settling, or otherwise separating out. A further object of the invention was to provide hand dishwashing compositions which can comprise components that are unstable in customary dishwashing compositions

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in the presence of individual components normally present in such compositions.

It has surprisingly now been found that low water content dishwashing compositions, especially 5 those for washing kitchen- and tableware by hand, may be packaged economically in portions containing a dishwashing formulation in an amount dosed sufficiently for one wash, which may if desired, in a dishwashing composition portion, comprise components 1.0 homogeneous distribution in a large amount of the same composition in a bottle or in a container was impossible for a prolonged storage period in the prior art, and which, if desired, include components whose stability was low or at least inadequate in the presence of other components of the composition.

The invention provides a portion of a low water content cleaning composition comprising one or more enclosures comprising at least one water-soluble polymer material and at least one active washing formulation partly or fully surrounded by said at least one water-soluble polymer material. The cleaning composition is preferably a cleaning composition for cleaning hard surfaces, more preferably for the manual cleaning of hard surfaces, most preferably dishwashing composition in the form of portions.

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In the context of the present invention, the term "dishwashing composition portion" refers to a cleaning composition in an amount sufficient for a dishwashing operation which takes place in an aqueous phase. This may be, for example, a machine washing 30 operation, as accomplished using standard commercial dishwashers. In accordance with the invention, however, this term also embraces a dish wash (accomplished, for example, in a hand washbasin or in a bowl) or some other cleaning operation. In accordance with the invention, the present cleaning composition portions or dishwashing composition portions are preferably used for manual cleaning operations on kitchentableware. The term "dishwashing composition

subportion" refers in the context of the present invention to a component amount of a dishwashing composition portion which is present in a phase separate from other dishwashing composition subportions, in spatial communication with dishwashing composition subportions of dishwashing composition portion, and which by means of appropriate measures has been formulated in such a way that, separately from or else simultaneously with other 10 dishwashing composition subportions of t.he dishwashing composition portion, it may be placed into the wash liquor and may, if appropriate, be suspended dissolved therein. A dishwashing composition subportion may contain the same ingredients as another dishwashing composition subportion of the dishwashing composition portion; preferably, however, two dishwashing composition subportions of the same dishwashing composition portion contain different ingredients, especially different active washing formulations.

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accordance with the invention. the dishwashing composition portions comprise measured amounts of at least one active washing formulation, usually measured amounts of two or more active washing 25 formulations. It is possible for the portions to comprise only active washing formulations of one particular make-up. In accordance with the invention it is preferred, however, for two or more, usually at least two, active washing formulations of different make-up to be present in the dishwashing composition 30 portions. The make-up may be different in terms of the concentration of the individual components of the active washing formulation (quantitative) and/or in respect of the nature of the individual components of the active washing formulation (qualitative), It is 35 particularly preferred for the components to be adapted in terms of nature and concentration to the tasks which the dishwashing composition subportions are required to fulfill in the cleaning operation. In the context of

the present invention, the subportions are preferably the first, second and, if desired, third or even higher (fourth, fifth, etc.) measured amounts, embraced by identical or different water-soluble materials, of one or more active washing formulations which are combined into a cleaning or dishwashing composition portion in accordance with the invention.

Detailed Description of the Invention

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In the context of the present invention, the 10 term "active washing formulation" embraces formulations of all conceivable substances that are relevant in the context of a ware-cleaning operation. These substances are, primarily, the cleaning compositions themselves, with their individual components which are elucidated further in the ongoing course of the description. These include active substances such as surfactants (anionic, nonionic, cationic, and amphoteric surfactants). enzymes, special polymers, dyes, and fragrances (perfumes), without the term being limited to these groups of substances.

The term "active washing formulations" also, however, embraces cleaning assistants. Examples of these are solvents, solubilizers, UV stabilizers, soil repellants, i.e., polymers which counter redirtying of 25 hard surfaces, and silver protectants. In accordance with the invention, dishwashing composition additives such as rinse aids are also considered as active washing formulations.

In accordance with the invention, the cleaning composition portion or dishwashing composition portion 30 comprises one or more enclosures comprising one or more water-soluble polymer materials themselves comprising, in whole or in part, at least one active washing formulation. It is possible for the dishwashing composition portion to comprise an enclosure comprising 35 one or more water-soluble polymer materials, or for two or more enclosures to be present. In the context of the present invention, the presence of one enclosure is preferred, producing advantages in the context of the

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choice of material and also in respect of the requirement that the water-soluble polymer material must dissolve without residue in the cleaning or washing liquor. The enclosure(s) may be formed from a single water-soluble polymer material or from two or more different polymer materials. The use of two or more polymer materials is possible in principle. In the light of the present objective, the use of a single material is particularly preferred accordance with the invention, and it is this particularly which is addressed below.

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In one preferred embodiment of the invention, the water-soluble polymer material completely or partly surrounding said at least one active 15 formulation is a water-soluble pack. By this is meant a two- or three-dimensional component which partly or fully surrounds at least one active formulation. The exact form of such a pack is not critical and may substantially be adapted to the circumstances of use. Examples of suitable embodiments are polymer films or sheets worked into various forms (such as tubes, pillows, cylinders, bottles, disks or the like), capsules, and other conceivable forms. Particular preference is given in accordance with the 25 invention to films, which may be bonded and/or sealed to give packs such as tubes, pillows or the like, after having been filled with subportions of the dishwashing composition portions of the invention, or with the dishwashing composition portions of the invention 30 themselves.

Furthermore, preference is also given in accordance with the invention, owing to the outstanding adaptability of the properties to the desired physical conditions, to polymer film packs comprising water-soluble polymer materials. Films of this kind are known in principle from the prior art.

Suitable water-soluble polymer materials are in principle all polymer materials which under the prevailing conditions (temperature, pH, concentration - 7 -

of active washing components) are able to dissolve completely in the aqueous phase. With particular preference, the polymer materials may belong to the groups consisting of (acetalized) polyvinyl alcohol, polyvinylpyrrolidone, polyethylene oxide, gelatin, cellulose and derivatives thereof, and mixtures of said materials.

Polyvinyl alcohols (PVAL for short) are polymers of the general structure

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[-CH2-CH(OH)-]n

which also contain structural units of the type

[-CH2-CH (OH) -CH (OH) -CH2-]

in minor amounts. Since the corresponding monomer (vinyl alcohol) is unstable in free form, polyvinyl alcohols are prepared by way of polymer-analogous reactions by hydrolysis, but industrially in particular by alkali-catalyzed transesterification of polyvinyl acetates with alcohols, preferably methanol. These industrial processes also make it possible to obtain PVAL containing a predetermined residual fraction of acetate groups ("acetalized PVAL").

Standard commercial PVAL (e.g., Mowiol* grades from Hoechst) are commercialized as yellowish white powders or granules having degrees of polymerization in the range of approximately 500 to 2500 (corresponding to molecular masses of from approximately 20,000 to 100,000 g/mol) and have different degrees of hydrolysis of 98 to 99 or 87 to 89 mol*. They are, therefore, partially hydrolyzed polyvinyl acetates having a residual acetyl group content of from approximately 1 to 2 or from 11 to 13 mol*.

The water-solubility of PVAL may be reduced by aftertreatment with aldehydes (acetalization), by complexing with Ni salts or Cu salts, or by treatment with dichromates, boric acid and/or borax, and so

adjusted in a targeted manner to desired levels. PVAL films are substantially impervious to gases such as oxygen, nitrogen, helium, hydrogen, and carbon dioxide, but do allow the passage of water vapor.

Examples of suitable water-soluble PVAL films are those obtainable from Syntana Handelsgesellschaft E. Harke GmbH & Co. under the designation "SOLUBLON®". Their solubility in water can be adjusted with great precision, and in this product range there are films available which are soluble in the aqueous phase within all of the temperature ranges relevant for the application.

Polyvinylpyrrolidones, called PVPs for short, may be described by the following general formula:

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CH-CH₂

PVPs are prepared by free-radical addition polymerization of 1-vinylpyrrolidone. Standard commercial PVPs have molecular masses in the range from approximately 2500 to 750,000 g/mol and are sold as white, hygroscopic powders or as aqueous solutions.

Polyethylene oxides, PBOX for short, are polyalkylene glycols of the general formula

H-[O-CH2-CH2]n-OH 25 which are prepared industrially by base-catalyzed polyaddition of ethylene oxide (oxirane) into systems usually including small amounts of water, using ethylene glycol as the starter molecule. They have molecular masses in the range from approximately 200 to 30 5,000,000 g/mol, corresponding to degrees polymerization n of from approximately 5 to >100,000. Polyethylene oxides possess an extremely low concentration of reactive hydroxyl end groups and 35 exhibit only weak glycol properties.

Gelatin is a polypeptide (molecular mass: from approximately 15,000 to >250,000 g/mol) which is obtained principally by hydrolysis under acidic or alkaline conditions of the collagen that is present in animal bones and skin. The amino acid composition of gelatin corresponds substantially to that of the collagen from which it has been obtained, and varies depending on its provenance. The use of gelatin as a water-soluble coating material is extremely widespread, especially in pharmacology, in the form of hard or soft gelatin capsules. The use of gelatin in the form of films is minimal owing to its high price in comparison to the aforementioned polymers.

In the context of the present invention, preference is also given to dishwashing composition portions whose pack comprises water-soluble film comprising at least one polymer from the group consisting of starch and starch derivatives, cellulose and cellulose derivatives, especially methylcellulose, and mixtures thereof.

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Starch is a homoglycan in which the glucose units are linked a-glycosidically. Starch is composed of two components of different molecular weight: approximately 20 to 30% straight-chain amylose (MW 25 approximately 50,000 to 150,000) and 70 to 80% branched-chain amylopectin (MW approximately 300,000 to 2,000,000). Also present are small amounts of lipids, phosphoric acid, and cations. Whereas amylose forms long, helical, interlooped chains comprising approximately 300 to 1200 glucose molecules, owing to the 1,4 linkage, in the case of amylopectin the chain branches by 1,6 linkage, after on average 25 glucose units, to form a treelike structure comprising approximately 1500 to 12,000 molecules of glucose. In addition to 35 starch itself, starch derivatives obtainable by polymer-analogous reactions from starch also suitable for preparing water-soluble enclosures of the cleaning or dishwashing composition portions in the context of the present invention.

Examples of such chemically modified starches include products of esterifications and etherifications in which hydroxy hydrogen atoms have been substituted. Alternatively, starches in which the hydroxyl groups have been replaced by functional groups not attached via an oxygen atom may be used as starch derivatives. The group of the starch derivatives includes, for example, alkali metal starches, carboxymethyl starch (CCMS), starch esters and starch ethers, and amino starches.

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Pure cellulose has the formal empirical composition $(C_nH_{10}O_n)_n$ and, considered formally, is a β -1,4-polyacetal of cellubiose, which itself is constructed of two molecules of glucose. Suitable celluloses consist of from about 500 to 5000 glucose 15 units and, accordingly, have average molecular masses of from 50,000 to 500,000. Cellulose-based disintegrants which may be used in the context of the present invention also include cellulose derivatives obtainable from cellulose bv polymer-analogous 20 reactions. Such chemically modified celluloses include, products of esterifications example. etherifications in which hydroxy hydrogen atoms have been substituted. Alternatively, celluloses in which 25 the hydroxyl groups have been replaced by functional groups not attached via an oxygen atom may also be used as cellulose derivatives. The group of the cellulose derivatives embraces, for example, alkali celluloses, carboxymethylcellulose (CMC), cellulose 30 esters and cellulose ethers, and aminocelluloses.

Preferred water-soluble film enclosures comprise a polymer having a molecular mass of between 5000 and 500,000 daltons, preferably between 7500 and 250,000 daltons, and in particular between 10,000 and 100,000 daltons. The water-soluble film that forms the enclosure usually has a thickness of from 1 to 150 μm , preferably from 2 to 100 μm , with particular preference from 5 to 75 μm , and in particular from 10 to 50 μm .

These water-soluble films may be prepared by various techniques. Mention may be made in principle here of blow, calendering, and casting techniques. In one preferred technique, the films, starting from a melt, are blown with air via a blowing mandrel to form a tube. In the calendering technique, which is likewise one of the preparation techniques used with preference, plasticated the raw materials, by appropriate additives, are passed through nozzles to form the films. In this case it may be necessary in particular to follow passage through the nozzles by a drying operation. In the case of the casting technique, again one of the preferred preparation techniques, an aqueous polymer formulation is placed on a heatable drying roll, evaporation of the water is followed by optional cooling, and the film is taken off. If desired, this film is additionally powdered before or while it is taken off.

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Capsules as enclosures for the active washing 20 formulation(s) of the dishwashing composition portion of the invention are likewise prepared by techniques known from the prior art and may consist preferably of (optionally acetalized) PVAL or of gelatin, such as soft gelatin or hard gelatin, for example.

In one preferred embodiment of the invention, the one or more enclosures for the active washing formulation(s) comprise a PVAL film which is soluble in water at a certain temperature. A film of this kind may be processed advantageously by adhesive bonding, using a water-soluble adhesive, for example, or by heat sealing, to give enclosures for active washing formulations. The advantage of such a film enclosure is that its solubility in water may be adjusted precisely in respect of the desired temperature and that on introduction into the washing or cleaning liquor it dissolves rapidly and without residue, the active washing formulation(s) enclosed by the film being released rapidly into the washing or cleaning liquor. This is important precisely in the context of the

washing or cleaning of kitchen- and tableware by hand, since in contrast to machine dishwashing the mechanical agitation of the liquor is not automatic, but instead would have to be effected by the user.

5 In a further-preferred embodiment of invention, said at least one water-soluble polymer material of the enclosure(s) comprises one or more incorporated components of the active formulation(s). This concept is subject matter of earlier patent application DE 199 29 098.9, according 10 to which certain additives of active washing formulations, especially individual components which regulate the activity or else increase the user acceptance of the active washing formulation are present totally or predominantly, in 15 physically incorporated form, in the water-soluble polymer material of the enclosure. In accordance with the invention, such components which may be present incorporated in the polymer material of 20 enclosure(s) may be, for example, UV protection substances, dyes, fragrances, antibacterial agents, polymers such as, for example, a soil-repellant polymer, corrosion inhibitors, or bitter substances (the latter may prevent unauthorized persons, such as 25 children, from putting the enclosure(s) in their mouths), without being restricted to these examples. Provided the important properties of the enclosure such as its mechanical stability (even over a prolonged period) and its complete water-solubility are not adversely affected, one or more such additives in any desired combination and amount may be incorporated in the polymer material. Preferred amounts are from 0.1 to 10% by weight of the additive, based on the total weight of the film or capsule material, more preferably from 1 to 7% by weight, with very particular preference 35 from 3 to 6% by weight.

In view of the fact that at least one polymer material is used as enclosure(s) of the active washing formulation(s), the essential properties of said

material comprising its solubility in the aqueous medium used for washing, it is an essential feature of the present invention that the active washing formulation(s) of the dishwashing composition portion of the invention is (are) of low water content. "Of low water content" means that in all of its components the dishwashing composition portion contains as little free (and hence capable of reaction with the material of the enclosure(s)) water as possible. Preferably, the active washing formulation(s) has (have) water contents of less than 15% by weight, based on the total weight of the active washing formulation(s), more preferably water contents of less than 10% by weight.

In one preferred embodiment of the invention, 15 the components of the active washing formulation(s) are selected from the group consisting of anionic, nonionic, cationic and amphoteric surfactants, nonaqueous carriers, enzymes, dyes, fragrances, antibacterial agents, polymers, and rinse aids, the stated amounts referring in each case to the total 20 weight of the active washing formulation(s).

Substances which may also be used ingredients of cosmetic compositions may be referred to below in accordance with the International Nomenclature of Cosmetic Ingredients (INCI) nomenclature. Chemical 25 compounds bear an INCI name in English, while plant ingredients are listed exclusively in Latin accordance with Linné. So-called trivial names such as "water". "honey" or "seasalt" are likewise given in The TNCT names can be found the "International Cosmetic Ingredient Dictionary and Handbook, Seventh Edition (1997)", which is published by The Cosmetic, Toiletry and Fragrance Association (CTFA), 1101, 17th Street NW, Suite 300, Washington, DC 20036, USA, and contains more than 9000 INCI names plus 35 references to more than 37,000 commercial names and designations, including the technical relevant distributors from over 31 countries. The International Cosmetic Ingredient Dictionary and Handbook assigns the

ingredients to one or more chemical classes, examples being "polymeric ethers", and one or more functions, examples being "surfactants - cleansing agents", which it elucidates further in turn. In the text below, reference may likewise be made to these classifications.

In order to develop a good cleaning performance in the course of washing, the dishwashing composition portions of the invention may comprise surface-active substances from the group consisting of anionic, nonionic, cationic and amphoteric or zwitterionic surfactants. Anionic surfactants are particularly preferred on economic grounds and on the basis of their performance spectrum. Surfactants from the individual groups may be used as individual substances. It is preferred to use mixtures of surfactants, advantageously mixtures of surfactants from two or more of the abovementioned groups.

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Anionic surfactants in accordance with the present invention may be aliphatic sulfates such as 20 fatty alcohol sulfates, fatty alcohol ether sulfates, dialkyl ether sulfates, monoglyceride sulfates, and also aliphatic and aromatic sulfonates such as alkanesulfonates, olefinsulfonates, ether sulfonates, 25 n-alkvl ether sulfonates, ester sulfonates, ligninsulfonates, and alkylbenzenesulfonates. Likewise possible for use in the context of the present invention are fatty acid cyanamides, sulfosuccinic esters, fatty acid isethionates, acylaminoalkane-(fatty acid taurides). fattv 30 sulfonates sarcosinates, ether carboxylic acids, and alkyl (ether) phosphates.

Preferred alk(en)yl sulfates are the alkali metal salts and especially the sodium salts of the sulfuric monoesters of C₁₂-C₁₈ fatty alcohols, for example those of coconut fatty alcohol, tallow fatty alcohol, lauryl, myristyl, cetyl or stearyl alcohol, or of the C₁₀-C₂₀ oxo alcohols, and the monoesters of secondary alcohols (secondary alkyl sulfates, SAS) of

these chain lengths. Preference is also given to alk(en)yl sulfates of said chain length which contain a synthetic straight-chain alkyl radical prepared on a basis, these petrochemical sulfates possessing degradation behavior similar to that of the appropriate compounds based on fatty chemical raw materials. From a wash technology standpoint, the C12-C16 alkyl sulfates and C12-C15 alkyl sulfates, and also C14-C15 alkyl sulfates, are preferred. Suitable secondary alkyl sulfates include 2- and/or 3-alkyl sulfates and also, desired, higher homologues (4-, 5-, sulfates, etc.), are preparable, for example, in accordance with US Patent 3,234,258 or 5,075,041, and are obtainable as commercial products from the Shell Oil Company under the name DAN®, examples being the US Patent 5,529,724 and H 1,665 products DAN 214, a C14 SAS containing 99% 2- and 3-alkyl sulfate, DAN 216, a C16 SAS containing 99% 2- and 3-alkyl sulfate, and DAN 100, a SAS containing 62% 2- and 3-alkyl sulfate. Particular preference is given in the context

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of the present invention to the fatty alcohol ether sulfates. Fatty alcohol ether sulfates are products of sulfating reactions with alkoxylated alcohols. In this context, the skilled worker generally understands by 25 the term "alkoxylated alcohols" the reaction products of one or more alkylene oxides, preferably ethylene oxide, with alcohols, in the context of the present preferably the relatively long-chain invention alcohols, examples being the straight-chain or branched alcohols having chain lengths from C7 to C21 such as 2-methyl-branched C9 to C11 fatty alcohols containing on average 3.5 EO or the C_{12} to C_{18} fatty alcohols containing from 1 to 4 EO. In general, depending on the reaction conditions, n mols of ethylene oxide and one mol of alcohol give a complex mixture of addition products with different degrees of ethoxylation. A further embodiment comprises using mixtures of the alkylene oxides, preferably the mixture of ethylene oxide and propylene oxide. Very particular preference

is given in the context of the present invention to fatty alcohols with low degrees of ethoxylation (from 0.5 to 4 mol EO, preferably from 1 to 2 EO).

Suitable surfactants of the sulfonate type are preferably alkylbenzenesulfonates, olefinsulfonates, i.e., mixtures of alkene- and hydroxyalkenesulfonates, and also disulfonates, as obtained, for example, from C12-18 monopolefins with a terminal or internal double bond by sulfonation with gaseous sulfur trioxide and subsequent alkaline or acidic hydrolysis of the sulfonation products. Alkylbenzenesulfonates for the purposes of the teaching of the invention alkylbenzenesulfonates containing straight-chain or branched, saturated or unsaturated C6-22 alkyl radicals, preferably C8-18 alkyl radicals, especially C9-14 alkyl radicals, very preferably C10-13 alkyl radicals. They are used in the form of alkali metal salts and/or alkaline earth metal salts, especially sodium, potassium, magnesium and/or calcium salts, and also as ammonium salts or mono-, di- or trialkanolammonium salts, 20 mono-, di- or triethanolpreferably and/or -isopropanolammonium salts, in particular mono-, ditriethanolammonium salts. but also as alkvlbenzenesulfonic acid together with the corresponding alkali metal hydroxide and/or alkaline earth metal hydroxide and/or ammonia and/or mono-, dior trialkanolamine. In one particularly preferred the dishwashing composition embodiment portions mono-, diand/or trialkanolammonium comprise alkylbenzenesulfonate, especially monoethanolammonium alkylbenzenesulfonate, in amounts of from 10 to 100% by weight, preferably from 30 to 100% by weight, in particular from 50 to 100% by weight, based on the total amount by weight of alkylbenzenesulfonates. With particular preference, the dishwashing portions in 35 as accordance with the invention comprise, alkylbenzenesulfonates, exclusively mono-, di- and/or trialkanolammonium alkylbenzenesulfonate, more preferably exclusively monoethanolammonium alkylbenzenesulfonate. Also suitable are alkanesulfonates obtained from C12-18 alkanes by means, for example, of sulfochlorination or sulfoxidation with subsequent hydrolysis or neutralization, respectively. Likewise suitable are the esters of 2-sulfo fatty acids (ester sulfonates), e.g., the 2-sulfonated methyl esters of hydrogenated coconut, palm kernel or tallow fatty acids.

The anionic surfactants are used preferably in amounts of between 0.2 and 80% by weight, preferably in amounts of from 10 to 70% by weight, with particular preference from 25 to 60% by weight, very preferably from 40 to 60% by weight.

Particularly suitable surfactant comprise those of anionic surfactants in combination with one or more nonionic surfactants or betaine surfactants, the betaine surfactants in this context being equivalent to the class of the amphoteric surfactants. The conjoint additional use of nonionic surfactants and betaine surfactants in a mixture may also be advantageous for many applications.

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Nonionic surfactants in the context of the invention may be alkoxylates, present polyglycol ethers, fatty alcohol polyglycol ethers, endgroup-capped alkylphenol polyglycol ethers, polyglycol ethers, mixed ethers and hydroxy-mixed ethers, and fatty acid polyglycol esters. It is likewise possible to use ethylene oxide, propylene oxide, block polymers, fatty acid alkanolamides, and fatty acid polyglycol ethers. An important class of nonionic surfactants which may be used in accordance with the invention is that of the polvol surfactants and, of these, especially the glycosurfactants, such as alkyl polyglycosides and fatty acid glucamides. The 35 alkyl polyglucosides are particularly preferred.

Nonionic surfactants used are preferably alcohol alkoxylates, i.e., alkoxylated, advantageously ethoxylated, especially primary, alcohols having preferably 8 to 18 carbon atoms and on average from 1

to 12 mol of ethylene oxide (EO) per mol of alcohol, in which the alcohol radical may be linear or methylbranched, preferably in position 2, and/or may comprise linear and methyl-branched radicals in a mixture, as are commonly present in oxo alcohol radicals. In particular, however, preference is given to alcohol ethoxylates containing linear radicals from alcohols of natural origin having 12 to 18 carbon atoms, e.g., from coconut, palm, tallow fatty or oleyl alcohol, and on average from 2 to 8 EO per mol of alcohol. Preferred 10 ethoxylated alcohols include, for example, C12-14 alcohols containing 3 EO or 4 EO, Co.11 alcohol containing 7 EO, C13-15 alcohols containing 3 EO, 5 EO, 7 EO or 8 EO, C12-18 alcohols containing 3 EO, 5 EO or 7 EO, and mixtures of these, and also mixtures of C12-14 alcohol containing 3 EO and C12-18 alcohol containing The stated degrees of ethoxylation statistical mean values, which for a specific product may be an integer or a fraction. Preferred alcohol 20 ethoxylates have a narrowed homologue distribution (narrow range ethoxylates, NREs). In addition to these nonionic surfactants it is also possible to use fatty alcohols containing more than 12 EO. Examples thereof are tallow fatty alcohol containing 14 EO, 25 EO, 30 EO or 40 EO. 25

A further class of nonionic surfactants used with preference, which are used either as sole nonionic surfactant or in combination with other nonionic surfactants, is that of alkoxylated, preferably 30 ethoxylated, or ethoxylated and propoxylated, fatty acid alkyl esters, preferably with 1 to 4 carbon atoms in the alkyl chain, especially fatty acid methyl esters, as described, for example, in Japanese Patent Application JP 58/217598 or those prepared preferably by the process described in International Patent Application WO-A-90/13533.

A further class of nonionic surfactants which may be used with advantage are the alkyl polyglycosides (APGs). Alkyl polyglycosides are surfactants which may

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be obtained by reacting sugars and alcohols in accordance with the relevant techniques of preparative organic chemistry, where depending on the mode of preparation a mixture of monoalkylated, oligomeric or polymeric sugars is produced. Preferred polyglycosides may be alkyl polyglucosides, particular preference given to those where the alcohol is a long-chain fatty alcohol or is a mixture of longchain fatty alcohols with branched or unbranched alkyl 10 chain lengths of between Co and Clo and the degree of oligomerization of the sugars is between 1 and 10. Alkyl polyglycosides which may be used with advantage satisfy the general formula RO(G)z, where R is a linear or branched radical, especially one which is methylbranched in position 2, and is 15 saturated unsaturated. aliphatic, and contains 8 22. preferably 12 to 18, carbon atoms, and G is the symbol which represents a glycose unit having 5 or 6 carbon atoms, preferably glucose. The degree of glycosidation, z, is between 1.0 and 4.0, preferably between 1.0 and 20

Particular preference is given to the use of the alkyl polyglycosides, especially alkyl polyglucosides, in amounts of from 0.1 to 15.0% by 25 weight, preferably in amounts of from 0.2 to 10.0% by weight, more preferably in amounts of from 0.5 to 8.0% by weight, and with particular preference in amounts of from 1.0 to 6.0% by weight.

2.0, and in particular between 1.1 and 1.4.

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Nonionic surfactants of the amine oxide type and of the fatty acid alkanolamide type may also be suitable. The amount of these nonionic surfactants is preferably not more than that of the ethoxylated fatty alcohols, in particular not more than half thereof.

The amine oxides that are suitable in accordance with the invention include alkylamine oxides, especially alkylamicbumine oxides, and alkoxyalkylamine oxides. Preferred amine oxides satisfy the formula R12R3NT-0-, where R1 is saturated or unsaturated Cc-22 alkyl radical,

preferably C_{0-16} alkyl radical, in particular a saturated C_{10-16} alkyl radical, for example, a saturated C_{10-16} alkyl radical, which in the alkylamidoamine oxides is attached via a carbonylamidoalkylene group $-CO-NN-(CH_2)_z$ and in the alkoxyalkylamine oxides is attached via an oxealkylene group $-O-(CH_2)_z$ to the nitrogen atom N, z in each case being a number from 1 to 10, preferably from 2 to 5, especially 3, and R^2 and R^3 independently of one another are each an unsubstituted or hydroxyl-substituted C_{1-4} alkyl radical such as, for example, a hydroxyethyl radical, especially a methyl radical,

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Examples of suitable amine oxides are the following compounds, named in the INCI nomenclature: Almondamidopropylamine Oxide, Babassuamidopropylamine 15 Oxide, Behenamine Oxide, Cocoamidopropyl Amine Oxide, Cocamidopropylamine Oxide, Cocamine Oxide. Coco-Morpholine Oxide, Decylamine Oxide. Decyltetradecylamine Oxide, Diaminopyrimidine Oxide, 20 Dihydroxyethyl C8-10 Alkoxypropylamine Oxide. Dihydroxyethyl C9-11 Alkoxypropylamine Oxide. Dihydroxyethyl C12-15 Alkoxypropylamine Oxide, Dihydroxyethyl Cocamine Oxide, Dihydroxyethyl Lauramine Oxide, Dihydroxyethyl Stearamine Oxide, Dihydroxyethyl Tallowamine Oxide, Hydrogenated Palm Kernel Amine 25 Oxide, Hydrogenated Tallowamine Oxide, Hydroxyethyl Hydroxypropyl C12-15 Alkoxypropylamine Isostearamidopropylamine Oxide. Isostearamidopropyl Morpholine Oxide, Lauramidopropylamine Oxide, Lauramine Oxide, Methyl Morpholine Oxide, Milkamidopropyl Amine 30 Oxide, Minkamidopropylamine Oxide. Myristamidopropylamine Oxide, Myristamine Oxide. Myristyl/Cetyl Amine Oxide, Oleamidopropylamine Oxide, Oleamine Oxide, Olivamidopropylamine Oxide, 35 Palmitamidopropylamine Oxide, Palmitamine Oxide, PEG-3 Lauramine Oxide, Potassium Dihydroxyethyl Cocamine Oxide Phosphate, Potassium Trisphosphonomethylamine Oxide, Sesamidopropylamine Oxide, Soyamidopropylamine Oxide, Stearamidopropylamine Oxide, Stearamine Oxide,

Tallowamidopropylamine Oxide, Tallowamine Oxide, Undecylenamidopropylamine Oxide and Wheat Germamidopropylamine Oxide. Preferred amine oxide(s) is (are), for example, Cocamine Oxide (N-Cocoalkyl-N,N-5 dimethylamine oxide), Dihydroxyethyl Tallowamine Oxide (N-tallowalkyl-N,N-dihydroxyethylamine oxide) and/or Cocamidopropylamine Oxide (cocoamidopropylamine oxide), especially Cocamidopropylamine Oxide.

Further suitable surfactants are polyhydroxy 10 fatty acid amides of the formula (I)

R1 | R-CO-N-[Z]

(1)

where RCO is an aliphatic acyl radical having 6 to 22
15 carbon atoms, R¹ is hydrogen or an alkyl or
hydroxyalkyl radical having 1 to 4 carbon atoms, and
[Z] is a linear or branched polyhydroxyalkyl radical
having 3 to 10 carbon atoms and from 3 to 10 hydroxyl
groups. The polyhydroxy fatty acid amides are known
20 substances which are customarily obtainable by
reductive amination of a reducing sugar with ammonia,
an alkylamine or an alkenylamine, and subsequent
acylation with fatty acid, a fatty acid alkyl ester or
a fatty acid chloride.

The group of the polyhydroxy fatty acid amides also includes compounds of the formula (II)

R1-0-R-CO-N-[Z]

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(II)

30 where R is a linear or branched alkyl or alkenyl radical having 7 to 12 carbon atoms, R¹ is a linear, branched or cyclic alkyl radical or an aryl radical having 2 to 8 carbon atoms and R² is a linear, branched or cyclic alkyl radical or an aryl radical or an oxyalkyl radical having 1 to 8 carbon atoms, preference being given to C₁₋₄ alkyl radicals or phenyl radicals.

and [Z] is a linear polyhydroxyalkyl radical whose alkyl chain is substituted by at least two hydroxyl groups, or alkoxylated, preferably ethoxylated or propoxylated, derivatives of said radical.

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is preferably obtained by reductive [Z] amination of reduced sugar, e.g., glucose, fructose, maltose, lactose, galactose, mannose or xylose. The N-alkoxy- or N-aryloxy-substituted compounds may then be converted to the desired polyhydroxy fatty acid amides by reaction with fatty acid methyl esters in the presence of an alkoxide as catalyst, for example according to the teaching of international application WO-A-95/07331.

Preferably. nonionic surfactants are 15 overall in amounts of from 1 to 80% by weight, preferably from 5 to 30% by weight, with particular preference from 7 to 35% by weight, and very preferably from 10 to 25% by weight.

The zwitterionic surfactants or amphoteric 20 surfactants which may be used in accordance with the invention include the betaines and the alkylamido alkylamines (INCI alkylamido alkylamines), and also the alkyl-substituted amino acids (INCI Alkyl-Substituted Amino Acids), especially the aminopropionates, the acylated amino acids, and the biosurfactants. A preferred ingredient is betaine, especially alkylamidobetaine.

Suitable betaines are the alkyl betaines, the alkylamido-betaines, the imidazolinium betaines, the 30 sulfobetaines (INCI sultaines). and the phosphobetaines, and they preferably satisfy the formula (III)

R^{1} -[CO-X-(CH₂)₀]_x-N⁺(R²)(R³) -(CH₂)m-[CH(OH) -CH₂]_{x-Y}-(III)

where R^1 is a saturated or unsaturated C_{6-22} alkyl radical, preferably C8-18 alkyl radical, in particular a saturated C10-16 alkyl radical, for example, a saturated C12-14 alkyl radical,

	- 23 -
	X is NH, NR 4 with the C_{1-4} alkyl radical R^4 , 0 or S,
	<pre>n is a number from 1 to 10, preferably from 2 to 5, especially 3,</pre>
5	x is 0 or 1, preferably 1,
	\mathbb{R}^2 , \mathbb{R}^3 independently of one another are an
	unsubstituted or hydroxyl-substituted C_{1-4}
	alkyl radical such as, for example, a
	hydroxyethyl radical, but especially a methyl
10	radical,
	m is a number from 1 to 4, especially 1, 2 or
	3,
	y is 0 or 1, and
	Y is COO, SO ₃ , OPO(OR^5)O or P(O)(OR^5)O, where R^5
15	is a hydrogen atom H or a C1-4 alkyl radical.
	The alkyl betaines and alkylamidobetaines,
	betaines of the formula (I) with a carboxylate group
	(Y = COO), are also called carbobetaines.
	Preferred amphosurfactants are the
20	alkylbetaines of the formula (IIIa), the
	alkylamidobetaines of the formula (IIIb), the
	sulfobetaines of the formula (IIIc), and the
	amidosulfobetaines of the formula (IIId):
	aminoparitoheratures of the formula (iiid):

25	R ¹ -N ⁺ (CH ₃) ₂ -CH2COO ⁻	(IIIa)
	R ¹ -CO-NH-(CH ₂) ₃ -N ⁺ (CH ₃) ₂ -CH ₂ COO ⁻	(IIIb)
	R ¹ -N ⁺ (CH ₃) ₂ -CH ₂ CH(OH)CH ₂ SO ₃ ⁻	(IIIc)
	R ¹ -CO-NH-(CH ₂) ₃ -N ⁺ (CH ₃) ₂ -CH ₂ CH(OH)CH ₂ SO ₃ -	(IIId)

30 where R1 is as defined for formula (I).

Particularly preferred amphosurfactants are the carbobetaines, especially the carbobetaines of the formulae (IIIa) and (IIIb), very preferably the alkylamidobetaines of the formula (IIIb).

35 Examples of suitable betaines and sulfobetaines are the following compounds, named in accordance with the INCI nomenclature: Almondamidopropyl Apricotamidopropyl Betaine, Avocadamidopropyl Betaine, Babassuamidopropyl Betaine, Behenamidopropyl Betaine,

Behenyl Betaine, Betaine, Canolamidopropyl Betaine, Capryl/Capramidopropyl Betaine, Carnitine. Betaine, Cocamidoethyl Betaine, Cocamidopropyl Betaine, Cocamidopropyl Hydroxysultaine, Coco-Betaine, Hydroxysultaine, Coco/Oleamidopropyl Betaine, Coco-Sultaine, Decvl Betaine. Dihydroxyethyl Glycinate, Dihydroxyethyl Soy Glycinate, Dihydroxyethyl Stearyl Glycinate, Dihydroxyethyl Tallow Glycinate, Dimethicone Propyl PG-Betaine. Erucamidopropyl Hydroxysultaine, Hydrogenated Tallow Betaine. Isostearamidopropyl Betaine, Lauramidopropyl Betaine, Lauryl Betaine. Lauryl Hydroxysultaine, Lauryl Sultaine, Milkamidopropyl Betaine, Minkamidopropyl Betaine, Myristamidopropyl Betaine, Myristyl Betaine, 15 Oleamidopropyl Betaine, Oleamidopropyl Hydroxysultaine, Oleyl Betaine, Olivamidopropyl Betaine, Palmamidopropyl Betaine, Palmitamidopropyl Betaine, Palmitoyl Carnitine, Palm Kernelamidopropyl Betaine, Polytetrafluoroethylene Acetoxypropyl Betaine, 20 Ricinoleamidopropyl Betaine, Sesamidopropyl Betaine, Sovamidopropyl Betaine, Stearamidopropvl Betaine, Stearvl Betaine, Tallowamidopropyl Betaine, Tallowamidopropyl Hydroxysultaine, Tallow Betaine, Tallow Dihydroxyethyl Betaine, Undecylenamidopropyl 25 Betaine and Wheat Germamidopropyl Betaine. A preferred is, for example, Cocamidopropyl (cocoamidopropvl betaine).

Preferably, these amphosurfactants are used in amounts of between 0.1 and 14.9% by weight, preferably from 0.5 to 8% by weight, and with particular preference from 1 to 6% by weight.

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In one preferred embodiment of the invention, the dishwashing composition portion comprises as surfactant mixture (a) from 0.2 to 80% by weight, preferably from 10 to 70% by weight, with particular preference from 25 to 60% by weight, very preferably from 40 to 60% by weight, of one or more anionic surfactants, preferably alkylbenzenesulfonate(s) and/or fatty alcohol ether sulfate(s), (b) from 1 to 80% by

weight, preferably from 5 to 50% by weight, with particular preference from 7 to 35% by weight, and very preferably from 10 to 25% by weight, of one or more nonionic surfactants, preferably alcohol alkoxylate(s), polyglycoside(s) and/or amine especially alcohol alkoxylate(s) or combinations of alcohol alkoxylate(s) with alkyl polyglycoside(s) and/or amine oxide(s), and (c) from 0.1 to 14.9% by weight, preferably from 0.5 to 8% by weight, and with particular preference from 1 to 6% by weight, of one or more betaine surfactants, preferably

alkvlamidobetaines. In addition to or instead of the inventive water content of preferably less than 15% by weight, based on the total weight of the active washing 15 formulation(s), and in particular less than 10% by weight, the active washing formulation(s) preferably comprise(s) one or more nonagueous Preferably, the nonaqueous carrier(s) is (are) soluble in water or miscible with water, and at least one, in 20 particular each, nonagueous carrier is liquid at room temperature (20°C).

The nonaqueous carrier(s) serve(s) (i) as a filler component for making up the other components of 25 the active washing formulation(s) to the desired portion amount, (ii) to control the fluidity or flow behavior, especially the viscosity, of the active washing formulation(s), (iii) to control the solubility or solubility behavior, especially the dissolution 30 rate, of the active washing formulation(s) in aqueous media, and/or (iv) as solvents or solubilizers (hydrotropic agents) for other components of the active washing formulation(s).

Examples of suitable nonaqueous carriers are solvents and polyalkylene glycols. In the context of the teaching of the invention, polyalkylene glycols are the tetramers and higher representatives, whereas in accordance with the invention the dimers and trimers belong to the solvents.

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Preferred solvents comprise one or more hydroxyl groups OH, one or more ester groups CO-O-C, and/or one or more ether groups C-O-C, preferably one or more hydroxyl groups, or one or more hydroxyl groups and one or more ether groups.

In particular, solvents in the context of the nonaqueous carrier components of the invention are used as a hydrotropic agent, viscosity regulator and/or lowtemperature stabilizer. They have a solubilizing especially for surfactants and perfume/fragrance and dye, and thus contribute to the incorporation of these components; prevent formation of liquid-crystalline phases, and contribute to forming clear products. The viscosity goes down as the amount of solvent goes up. Finally, the lowtemperature cloud point and clearing point fall as the amount of solvent increases.

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Particularly preferred solvents are, example, saturated or unsaturated, preferably 20 saturated, branched or unbranched C1-20 hydrocarbons, preferably C2-15 hydrocarbons, having at least one hydroxyl group and, if desired, one or more ether functions C-O-C, i.e., oxygen atoms which interrupt the carbon atom chain, with not more than 8, preferably not more than 6, in particular not more than 4, carbon being connected to one another without interruption by an ether function.

Such solvents include the following compounds, possibly monoetherified with a $C_{1.6}$ alkanol: $C_{2.6}$ alkylene glycols and poly- $C_{2.3}$ alkylene glycol ethers having on average from 1 to 9, preferably 2 to 3, identical or different, preferably identical, alkylene glycol groups per molecule, especially 1,2-propylene glycol, and also the $C_{1.6}$ alcohols, preferably ethanol, n-propanol or iso-propanol (2-propanol), especially ethanol, and also glycerol.

Exemplary solvents are the following compounds, named with their INCI nomenclature: Alcohol (ethanol), Buteth-3, Butoxyethanol, Butoxypropanol, n-Butyl

Alcohol, t-Butyl Alcohol, Butylene Glycol. Butyloctanol, Diethylene Glycol, Dimethoxydiglycol, Dimethyl Ether, Dipropylene Glycol, Ethoxydiglycol, Ethoxyethanol. Ethyl Hexanediol, 5 (ethyleneglycol), Hexanediol, 1,2,6-Hexanetriol, Hexyl Alcohol. Hexylene Glycol, Isobutoxypropanol, Isopentyldiol, Isopropyl Alcohol (iso-propanol), 3-Methoxybutanol, Methoxyethanol, Methoxymethylbutanol, Methoxy PEG-10, Methylal, Methyl Alcohol, Methyl Hexyl Ether. Methylpropanediol. Neopentyl Glycol, Methyl Ether, Pentylene Glycol, PPG-2-Buteth-3, Propanediol, Propyl Alcohol (n-propanol), Propylene Propylene Glycol Butyl Ether,

Tetrahydrofurfuryl Alcohol, Trimethylhexanol.

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Further particularly preferred solvents are the 15 monomeric or homopolymeric or heteropolymeric, especially monomeric and also homodimeric and homotrimeric, C2-C4 alkylene glycols which etherified with aliphatic C1-6 alcohols or aromatic 20 alcohols, e.g., methanol, ethanol. n-propanol. n-butanol, tert-butanol or phenol, or which are esterified with carboxylic acids, e.g., acetic acid, or carbonic acid, examples of such compounds being the products sold under the trade name Dowanol by the company Dow Chemical and those sold under the trade 25 names Arcosolv and Arconate by the company Arco Chemical and designated below by their INCI name, e.g., Butoxydiglycol (Dowanol DB), Methoxydiglycol (Dowanol DM), PPG-2 Methyl Ether (Dowanol DPM), PPG-2 Methyl Ether Acetate (Dowanol® DPMA), PPG-2 Butyl Ether 30 (Dowanol* DPnB), PPG-2 Propyl Ether (Dowanol* DPnP), Butoxyethanol (Dowanol® EB), Phenoxyethanol (Dowanol® EPh), Methoxyisopropanol (Dowanol PM), PPG-1 Methyl Ether Acetate (Dowanol PMA), Butoxyisopropanol 35 (Dowanol® PnB), Propylene Glycol Propyl Ether (Dowanol® PnP), Phenoxyisopropanol, (Dowanol* PPh), PPG-3 Methyl Ether (Dowanol TPM) and PPG-3 Butyl Ether (Dowanol TPnB) and also Ethoxyisopropanol (Arcosolv PE), tert-Butoxyisopropanol (Arcosolv PTB), PPG-2 tert-Butyl

Ether (Arcosolv DPTB) and Propylene Carbonate (Arconate PC), especially Butoxyisopropanol (Dowanol PnB).

Solvents are used preferably in an amount of from 0.1 to 80% by weight, more preferably from 1 to 50% by weight, in particular from 5 to 40% by weight, with particular preference from 7 to 30% by weight, very preferably from 10 to 20% by weight.

Polyalkylene glycols (polyglycols, polyglycol ethers; INCI Chemical Class: Polymeric Ethers) are known, predominantly linear, but in some cases also branched, polyethers, which are polymers containing terminal hydroxyl groups. The polyalkylene glycols with relatively high molecular masses are polymolecular, i.e., they consist of collectives of macromolecules 15 with different molecular masses.

Preferred polyalkylene glycols are liquid at room temperature (20°C) and preferably have a melting point of not above 20°C, in particular not above 15°C, with particular preference not above 10°C, and very preferably not above 5°C or even not above 0°C. The melting point in this context is the temperature at the point of transition from the solid to the liquid state. Where not stated below, the melting point of a 25 particular polyalkylene glycol is usually known from the literature or routinely determinable in accordance with one of the customary methods of melting point determination.

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The molecular masses of the polyalkylene 30 glycols are preferably in the range from 200 to 5000, in particular from 300 to 4000, with particular preference from 400 to 3000, and very preferably from 500 to 2000. In the case of the various polyalkylene glycols described below, certain ranges may be particularly advantageous.

Preferred in accordance with the invention are linear or branched, especially linear, polyalkylene glycols of the general formula HO-[R-O],-H, where R is (CH2)2, CH2CH(CH3) and/or (CH2)4 and n represents values or average values of from 4 to about 100, which are preparable by ring-opening polymerization of ethylene oxide, propylene oxide and/or tetrahydrofuran. Specifically, these are the polyethylene glycols where $R = (CH_2)_2$, the polypropylene glycols where $R = (CH_2)_4$, the polytetrahydrofurans where $R = (CH_2)_4$, and the copolymers of ethylene oxide, propylene oxide and/or tetrahydrofuran.

Preference is given in accordance with the invention to polyethylene glycols (PEG) having an average relative molecular mass of up to about 4000. Ultimately, PEGs with molecular masses above 4000 are all no longer liquid and therefore less suitable in accordance with the invention. Very preferably, the molecular masses of the polyethylene glycols are not 15 only not more than 2000 but indeed are only up to 1500, in particular only up to 1000 or even only up to 800. for example, 400 or 600. For polyethylene glycols there exist various nomenclatures, which can confusion. It is common in the art to state the average 20 relative molecular weight after the letters "PEG", so that "PEG 200" characterizes a polyethylene glycol having a relative molecular mass of from about 190 to about 210. In accordance with INCI nomenclature, the abbreviation PEG is given a hyphen and the hyphen is 25 followed directly by a number corresponding to the number n in the above general formula. Commercially available polyethylene glycols are, for example, PEG 200/PEG-4, PEG 300/PEG-6, PEG-7, PEG-8, PEG 400, PEG-9, PEG-10, PEG-12, PEG 600, PEG-14, PEG-16, PEG 800/PEG-18, PEG-20, PEG 1000, PEG 1200, PEG 1500/PEG-32, PEG-40, PEG 2000, PEG-55, PEG-60, PEG 3000, PEG 3350/PEG-75 and PEG 4000/PEG-90, the designations in accordance with the two nomenclatures being placed alongside one another separated by the symbol "/" for polyethylene 35 glycols which correspond to one another. commercially available polyethylene glycols are available, for example, under the trade names Carbowax (Union Carbide), Emkapol and Renex PEG (ICI), Lipoxol

(DEA), Polyglykol*E (Dow), Pluracol*E, Pluriol*E and Lutrol E (BASF), and Polydiol (Cognis). The company Clariant also markets polyethylene glycols. Sources of supply for the polyethylene glycols designated in accordance with INCI, which also serve as cosmetic ingredients, may be found in the International Cosmetic Ingredient Dictionary and Handbook.

Over a wide molecular mass range of from 250 (PPG-4) to 4000 (PPG-69), polypropylene glycols (PPG) are clear, virtually colorless liquids for whose designation the INCI nomenclature described above is used analogously. Thus the polypropylene glycols of the above general formula with values n of 5 and 6 are referred to as PEG-5 and PEG-6 respectively. The low molecular mass polypropylene glycols are miscible with water, whereas the representatives of higher molecular mass are less soluble in water. Available commercially, for example, are the INCI-designated polypropylene glycols PPG-7, PPG-9, PPG-12, PPG-13, PPG-15, PPG-17, 20 PPG-20, PPG-26, PPG-30, PPG-33, PPG-34, PPG-51 and PPG-69. Sources of supply may be found in the International Cosmetic Ingredient Dictionary and Handbook.

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copolymers preferably comprise random copolymers and, in particular, block copolymers of ethylene oxide and propylene oxide, ethylene oxide and tetrahydrofuran, propylene oxide and tetrahydrofuran, or ethylene oxide, propylene oxide and tetrahydrofuran, preferably of ethylene oxide and propylene oxide, with particular preference comprise block copolymers of 30 ethylene oxide and propylene oxide. The molecular masses of the copolymers are very preferably not only, as stated above, at least 500 but indeed at least about 1000.

Random copolymers which are preferred in accordance with the invention, comprising a ethylene oxide units and b propylene oxide units, are, for the following copolymers designated in example, accordance with the International Cosmetic Ingredient Dictionary and Handbook as PEG/PPG-a/b copolymers

(molecular mass), where a and b are averages: PEG/PPG-18/4 Copolymer (1000), PEG/PPG-17/6 Copolymer (1100), PEG/PPG-35/9 Copolymer (2100) and PEG/PPG-23/50 Copolymer (3900).

Inventively preferred block copolymers of 5 ethylene oxide and propylene oxide satisfy the formula $HO(CH_2CH_2O)_x(CH(CH_3)CH_2O)_y(CH_2CH_2O)_{x'}H$, where x and x' are averages from 2 to 130 and z represents averages from 15 to 67, and are designated with the international nonproprietary name Poloxamer, which is also used in the International Cosmetic Ingredient Dictionary and Handbook. Each poloxamer is characterized by a threedigit number. The first two digits, multiplied by 100, indicate the average molecular mass polypropylene glycol fraction, and the last digit, 15 multiplied by ten, indicates the polyethylene glycol fraction in % by weight. This is from 10 to 80% by weight, preferably not more than 50% by weight, in particular not more than 40% by weight, with particular 20 preference not more than 30% by weight, for example, 10, 20 or 30% by weight. The poloxamers are prepared in two stages, in the first of which propylene oxide is added onto propylene glycol in a controlled way and in the second of which the resultant polypropylene qlycol 25 block is framed by two polyethylene glycol blocks by addition of ethylene oxide. Examples of particularly preferred block copolymers are the following liquid poloxamer grades (x, y, x'; molecular mass; in some cases, melting point): Poloxamer 101 (2, 16, 2; 1100; -32), Poloxamer 122 (5, 21, 5; 1630; -26), Poloxamer 123 30 (7, 21, 7; 1900; -1), Poloxamer 105 (11, 16, 11; 1850; 7), Poloxamer 181 (3, 30, 3; 2000; -29), Poloxamer 124 (11, 21, 11; 2200; 16), Poloxamer 182 (8, 30, 8; 2500; -4), Poloxamer 183 (10, 30, 10; 2650; 10), Poloxamer 35 212 (8, 35, 8; 2750; -7), Poloxamer 231 (6, 39, 6; 2750; -37), Poloxamer 184 (13, 30, 13; 2900; 16), Poloxamer 185 (19, 30, 19; 3400), Poloxamer 282 (10, 47, 10; 3650; 7), Poloxamer 331 (7, 54, 7; 3800; -23), Poloxamer 234 (22, 39, 22; 4200; 18), Poloxamer 401 (6,

67, 6; 4400; 5), Poloxamer 284 (21, 47, 21; 4600) and Poloxamer 402 (13, 67, 13: 5000: 20). Commercially, the poloxamers are available under the trade names Pluronic and Symperonic PE, suffixed by a letter from the group L, P and F and by a two- or three-digit number. The last digit is identical with the last digit of the poloxamer nomenclature, and the aforementioned one- or two-digit numbers multiplied by 300 give the approximate molecular mass of the polypropylene glycol fraction and, respectively, multiplied by 3, approximately the number formed from the first two digits of the poloxamer nomenclature number, i.e., 3, 4, 6, 7, 8, 9, 10 and 12 in this sequence correspond to the two-digit numbers 10, 12, 18, 21, 23, 28, 33 and 40 at the beginning of the number in accordance with the poloxamer nomenclature. The letters distinguish liquid (L), pastelike (P), and solid (F) poloxamers. For example, poloxamer 101 is available as Pluronic L31 and Symperonic PE L31.

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A further class of suitable block copolymers of ethylene oxide and propylene oxide satisfy the formula HO (CH (CH3) CH2O) , (CH2CH2O) , (CH2CH (CH3) O) , H. Here, block is framed polvethylene qlycol by two polypropylene glycol blocks. whereas with the poloxamers a polypropylene glycol block is framed by two polyethylene glycol blocks. The preparation again takes place in two stages, in the first of which ethylene oxide is added onto ethylene glycol in a controlled way and in the second of which the resulting polyethylene glycol block is framed polypropylene glycol blocks by addition of propylene oxide. Commercially, these block copolymers available, like the poloxamers, under the trade name Pluronic (BASF), each followed by an alphanumeric code comprising three digits and the letter R inserted between the second and third digits. The connotation of the digits is identical with the connotation for the poloxamer nomenclature. The inserted letter R (for reverse) indicates the fact that the structure is inverted in comparison to the poloxamers. Preferred representatives of this class are the following Pluronic grades (molecular mass; melting point): Pluronic 10R5 (1950; 15), Pluronic 12R3 (1800; -20), Pluronic 17R1 (1900; -27), Pluronic 17R2 (2150; -25), Pluronic 17R4 (2650; 18), Pluronic 25R1 (2700; -5), Pluronic 25R2 (3100; -5), Pluronic 31R1 (3250; -25) and Pluronic 31R2 (3300; 9).

Polyalkylene glycols are used preferably in an 10 amount of from 0.1 to 80% by weight, more preferably from 1 to 40% by weight, in particular from 3 to 25% by weight, with particular preference from 5 to 15% by weight, very preferably from 7 to 10% by weight.

Nonaqueous carrier(s) is (are) used preferably in an amount of in total from 0.1 to 80% by weight, more preferably from 5 to 50% by weight, in particular from 10 to 40% by weight, with particular preference from 15 to 35% by weight, very preferably from 20 to 30% by weight.

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In one particular embodiment at least two nonaqueous carriers are used, in particular at least one solvent and at least one polyalkylene glycol, preferably in a weight ratio of solvent(s) to polyalkylene glycol(s) of from 10:1 to 1:10, in particular from 5:1 to 1:3, with particular preference from 3:1 to 1:2, and very preferably from 2:1 to 1:1.

In order to improve the cleaning action in the washing operation, especially in the case of stubborn residues, the dishwashing composition portions of the invention may include enzymes. Suitable enzymes are those from the class of the proteases, lipases, amylases, cellulases, and mixtures thereof. Especially suitable enzymatic active substances are those obtained from bacterial strains or fungi, such as Bacillus subtilis, Bacillus licheniformis, and Streptomyces griseus. Preference is given to the use of proteases of the subtilisin type, and especially to the use of proteases obtained from Bacillus lentus. Of particular interest in this context are mixtures of enzymes; for

example, of protease and amylase or protease and lipase or protease and cellulase or of cellulase and lipase or of protease, amylase and lipase, or protease, lipase and cellulase, but especially mixtures containing cellulase. Peroxidases or oxidases have also proven suitable in some cases. The enzymes may be adsorbed on carrier substances and/or embedded in coating substances in order to protect them against premature decomposition. With further preference, the enzymes are optimized for use under the conditions of machine washing, as regards, for example, the temperature of the washing operation. The proportion of enzymes, enzyme mixtures or enzyme granules in the dishwashing composition portions of the invention may amount, for example, to from about 0.1 to 5% by weight, preferably from 0.1 to about 2% by weight.

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Enzymes are added in accordance with the prior to multiphase cleaning product formulations. primarily cleaning product formulations such as machine 20 dishwashing compositions intended for the main wash cycle of a dishwasher. A disadvantage was that, again and again, problems occurred with the stability of the enzymes in the strongly alkaline aqueous medium. With the dishwashing composition portions of the invention 25 it is possible to use enzymes even in the context of a manual washing operation and so to utilize the cleaning action of enzymes to remove ware stains in the context of hand dishwashing as well. The enzyme component of an active washing formulation may be present in a form. separate from the other components or from other 30 components of the active washing formulation(s) that are harmful to the action of the enzyme, surrounded by an enclosure of a water-soluble polymer material, as a result of which the enzyme activity is retained even on 35 prolonged storage.

A further group of additives which is preferred in accordance with the invention comprises dyes, especially water-soluble or water-dispersible dyes. Preference is given here to dyes as commonly used to improve the visual appearance of cleaning products. The selection of such dyes causes no difficulties to the skilled worker, especially since such customary dyes possess high stability on storage and a high level of insensitivity toward the other ingredients of the active washing formulations, and toward light. In accordance with the invention, the dyes are present in the dishwashing composition portions in amounts of below 0.01% by weight.

10 Fragrances are added to the dishwashing composition portions of the invention in order to enhance the overall aesthetic appearance of the products and to provide the user not only with the technical performance (effective washing) but also with product which, sensorially, 15 is typical unmistakable. As perfume oils or fragrances it is possible to use individual odorant compounds, examples being the synthetic products of the ester, ether, aldehyde, ketone, alcohol. and hydrocarbon type. Examples of odorant compounds of the ester type are benzvl acetate, phenoxyethyl isobutyrate, p-tbutylcyclohexyl acetate, linalyl acetate, dimethylbenzylcarbinyl acetate, phenylethyl acetate, linalyl benzoate, benzyl formate, ethyl methylphenyl-25 glycinate, allyl cyclohexylpropionate, propionate, and benzyl salicylate. The ethers include, for example, benzyl ethyl ether. The aldehydes include, for example, linear alkanals having 8 to 18 carbon atoms, citral, citronellal, citronellyloxyacetaldehyde, 30 cyclamen aldehyde, hydroxycitronellal, lileal, bourgeonal.

The ketones include the ionones, α -isomethylionone, and methyl cedryl ketone. The alcohols include anethole, citronellol, Eugenol, geraniol, linalool, phenylethyl alcohol, and terpineol. The hydrocarbons include primarily terpenes such as limonene and pinene. Preference is given to mixtures of different odorants for use, matched to one another so that together they produce an appealing fragrance note.

Such perfume oils may also comprise natural mixtures of odorants, as are obtainable from plant sources. Examples are pine oil, citrus oil, jasmine oil, patchouli oil, rose oil, or ylang-ylang oil. Likewise suitable are muskatel oil, sage oil, camomile oil. clove oil, balm oil, mint oil, cinnamon leaf oil, lime blossom oil, juniperberry oil, vetiver oil, olive oil. galbanum oil and labdanum oil, and also orange blossom oil, neroliol, orange peel oil, and sandalwood oil.

The fragrance content is usually in the range up to 2% by weight of the overall dishwashing composition portion.

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The fragrances may be incorporated directly into the active washing formulations; alternatively, it may be advantageous to apply the fragrances to carriers which by means of a slower release of fragrance ensure a long-lasting fragrance during washing. Examples of such carrier materials which have proven suitable are cyclodextrins. The cyclodextrin-perfume complexes may additionally be coated with further auxiliaries. Since 20 such complexes are not soluble in the dishwashing compositions, their separate accommodation in an active washing formulation or even separate from the active washing formulations, in a separate enclosure with a water-soluble polymer material, is possible accordance with the invention.

The perfume and fragrance substances may in principle be present in each of the subportions (active washing formulations) of the dishwashing composition portions of the invention. With particular preference, however, they are present in a dishwashing composition subportion whose ingredients do not react undesirably with these components with concomitant decomposition or degradation.

As further additives in accordance with the invention, the dishwashing composition portions may also comprise polymers, for example, polymers which attach to hard surfaces (for example, to porcelain and glass), which have a positive effect on the capacity

for oil and fat to be washed off from these surfaces, and which therefore act specifically to counter redirtying (soil repellants). This effect particularly marked if a hard article (porcelain, glass) which has already been washed several times beforehand with a dishwashing composition of the invention comprising this oil- and fat-dissolving component becomes soiled. The preferred oil- and fatdissolving components include, for example, nonionic 10 cellulose ethers such as methylcellulose methylhydroxypropylcellulose having a methoxy group of from 15 to 30% by weight and a hydroxypropoxy group content of from 1 to 15% by weight, based in each case on the nonionic cellulose ether, and also the prior art polymers of phthalic acid and/or terephthalic acid and/or of derivatives thereof. especially polymers of ethylene terephthalates and/or polyethylene glycol terephthalates or anionically and/or nonionically modified derivatives of these. Of these, particular preference is given to the sulfonated 20 derivatives of phthalic acid polymers and terephthalic acid polymers.

Further conceivable components of the active washing formulations in the dishwashing composition 25 portions of the invention may, in one preferred embodiment, be agents having an antibacterial or bacteriostatic activity. Examples of suitable such compounds, individually or in appropriate combination, triclosan (2,4,4'-trichloro-2'-hydroxydiphenyl are: chloramine-T (N-chlorotoluenesulfonamide. 30 sodium salt), Germall 115 (imidazolidinylurea), sodium 2-phenoxyethanol, 1-phenoxy-2-propanol, 2-phenoxy-1-propanol, benzoic acid and its salts, lactic acid and its salts, salicylic acid and its salts, sorbic acid and its salts, and also natural and nature-identical plant extracts such as, for example, extracts from orange peel, pine oil, geraniol and nerol. When using the abovementioned salts of benzoic acid or of the carboxylic acids, suitable salts are primarily sodium, potassium, magnesium, and calcium

In further preferred embodiments, the dishwashing composition portions may comprise one or more additional components selected from the group consisting of solubilizers, UV stabilizers, defoamers, texturing agents, corrosion inhibitors, preservatives, silver protectants, and additives centle to the skin.

Advantages in respect of the clarity of the products are obtained, especially in the case of high surfactant content mixtures, by adding one or more dicarboxylic acids and/or their salts, alone or in a mixture, preferably a collocation of sodium salts of adipic, succinic and glutaric acid, to the formulation.

15 A collocation of this kind is obtainable, for example, under the trade name Sokalan* DSC Na. In this case it has been found particularly advantageous to use from 0.1 to 8% by weight, preferably from 1 to 6% by weight,

with particular preference from 2.5 to 5% by weight.

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A likewise advantageous effect in this respect in the compositions of the invention is brought about by the optional presence of solubilizers, especially for perfume and dyes, examples being alkanolamines and/or alkylbenzenesulfonates having 1 to 3 carbon atoms in the alkyl radical, especially cumene-, toluene- and xylenesulfonate, in amounts of up to 5% by weight, preferably from 0.05 to 3% by weight, in particular from 0.1 to 2% by weight.

A further group of additives which is preferred in the context of the invention comprises silver protectants. These agents comprise a large number of usually cyclic organic compounds which are likewise familiar to the skilled worker in question and which contribute to preventing the tarnishing of articles containing silver during the cleaning process. Specific examples may be benzotriazoles, triazoles and their complexes with metals such as Mn, Co, Zn, Fe, Mo, W or Cu, for example.

In addition to the ingredients mentioned so far, further ingredients customary in hand dishwashing compositions may be present, examples being UV stabilizers, defoamers (e.g., silicone oils, paraffin oils or mineral oils), texturing agents, corrosion inhibitors, preservatives, additives gentle to the skin, or the like, preferably in amounts of up to 5% by weight.

active washing formulations of 10 dishwashing composition portions of the invention may be prepared by stirring together the individual constituents in any order and leaving the mixture to stand until free from bubbles. The sequence of mixing is not critical for the preparation of the dishwashing composition portion in accordance with the invention.

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The active washing formulations accordingly may then be surrounded, in a manner known per se from the prior art, with enclosures comprising one or more water-soluble polymer materials. One preferred embodiment of the invention, for example, consists in providing an active washing formulation with a water-soluble polymer material enclosure forming a compartment or chamber. This may be, for example, a film cushion, a film pouch, or a capsule. In this case, therefore, the dishwashing composition portion, with all of the components of the active washing formulation that are necessary for the cleaning or wash cycle, are present in a self-contained compartment, which is sealed conventionally by adhesive bonding, welding, or in another way known from the prior art.

A further, likewise preferred embodiment of the dishwashing composition portion of the invention may comprise at least two active washing formulations enclosed by a water-soluble polymer material enclosure which forms at least two compartments. This embodiment may be advantageous, for example, when the dishwashing composition portion is intended to comprise individual components which immediately or else only on prolonged storage or else only on ingress of moisture or the like

undergo reactions with other components that lead to a reduction in the efficacy of the active washing formulation(s) overall or in connection with the efficacy of individual components. A typical example be enzymes, which in a strongly alkaline environment, and especially in the presence of water, undergo a loss of activity over time. In the same way, it is possible with this embodiment to add, to the active washing formulation, components which cannot be distributed uniformly in a larger volume of the finished product or which - despite initial uniform distribution - undergo sedimentation. These components may be admixed to an amount of the active washing formulation that is dosed for one wash cycle, or may be provided in a separate compartment or separate chamber which is connected to the compartment containing the other components of the active washing formulation.

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In principle, the amount of the active washing formulation(s) in a compartment or chamber of the 20 dishwashing composition portion is entirely arbitrary. Preferably, however, the compartment or compartments or chambers of the dishwashing composition portions of the invention contain an amount of at least 1 ml of one or more active washing formulations, more preferably an amount of from 1 to 10 ml of one or more active washing 25 formulations, with very particular preference an amount of from 1 to 5 ml of one or more active washing formulations.

Dishwashing composition portions in accordance 30 with the invention, packed for example in film cushions, welded film pouches, capsules, etc., can then be introduced into the cold or heated cleaning or washing liquor prior to a hand wash. The enclosure comprising the water-soluble polymer material(s) then dissolves rapidly and releases the active washing formulation(s) into the liquor.

In the form provided with the enclosure(s), the active washing formulations possess superior storage stability. Dosing of the active washing formulation

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into the liquor is reliable: under- or overdosing is systematically avoided. Where there are sensitive components in the active washing formulation(s), a reduction in their efficacy is prevented by the absence of interaction with other components of the active washing formulation. For example, the efficacy of enzymes is maintained, because they are held separately from alkaline components of the formulation(s) and are not added until the actual wash.

The invention is illustrated by the following examples without, however, being limited to them.

Examples

Dishwashing composition portions in accordance with the invention were prepared by stirring together the components indicated in the table below and dispensing the resulting formulations into cushions made from PVAL films (Solublon* PT from Synthana 20 Handelsgesellschaft E. Harke GmbH & Co.; heat-sealed) in an amount of 2 ml.

The dishwashing composition portions possessed good storage stability in the temperature range between 5 and 40°C. The washing and emulsifying properties were excellent. The films dissolved rapidly and without residue in water suitable for a hand wash, with a temperature of from 35 to 45°C.

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Table 1

Ex.	1	2	3	4	5	6	7	В	9
C _{18/13} ABS monoethanol-	30	30	34	34	34	34	34	-	-
amine salt									
C _{12/14} 2EO-FAES monoiso-	18	18	22.5	18	18	-	-	45	45
propanolamine salt									
C _{12/14} 1.3EO-FAES sodium	-	-	-	-	-	14	14	-	-
salt									
Cocoamidopropyl	4	-	4	2	2	2	2	2	-
betaine									
C _{12/16} alkyl poly-	-	-	-	2.5	2.5	2.5	2.5	2.5	5
glucoside (z=1.4)									
Cocoamidopropylamine	-	3	-	-	-	-	-	-	-
oxide									
C _{0/10} 5EO fatty alcohol	10	10	7.5	20	12.5	15	12.5	10	10
ethoxylate									
1,2-propylene glycol	19	19	-	-	-	-	10	19	19
Ethanol	-	-	13	-	-	7.5	-	-	-
Butoxyisopropanol	-	-	-	5	10	-	-	-	-
Polydiol 400	10	10	7	-	10	10	10	10	10
Polydiol 600	-	-	-	7.5	-	-	-	-	-
Perfume	1	1	1	1	1	1	1	1	1
Water	8	9	11	10	10	14	14	10.5	10

Remarks:

Amounts in % by weight active substance ABS = Alkylbenzenesulfonate FAES = Fatty alcohol ether sulfate Butoxyisopropanol = Dowanol® PnB Polydiol 400 = PEG 400 Polydiol 600 = PEG 600

What is claimed is:

- 1. A low water content cleaning composition portion comprising one or more enclosures comprising at least one water-soluble polymer material and at least one active washing formulation partly or fully surrounded by said at least one water-soluble polymer material
- 2. The composition portion as claimed in claim 1, wherein said at least one water-soluble polymer material of the enclosure(s) is selected from the group consisting of (optionally acetalized) polyvinyl alcohol, polyvinylpyrrolidone, polyethylene oxide, gelatin, cellulose and derivatives thereof, and mixtures of said materials.
- 15 3. The composition portion as claimed in claim 1 or 2, wherein said at least one water-soluble polymer material of the enclosure(s) is present in the form of film pouches or capsules.
- 4. The composition portion as claimed in any of claims 1 to 3, wherein said at least one water-soluble polymer material of the enclosure(s) comprises one or more incorporated components of the active washing formulation(s).
- 5. The composition portion as claimed in any of 5 claims 1 to 4, wherein the active washing formulation(s) has (have) water content of less than 15% by weight, (preferably < 10% by weight), based on the total weight of the active washing formulation(s).
 - 6. The composition portion as claimed in claim 5, wherein the water content is less than 10% by weight.
 - 7. The composition portion as claimed in any of claims 1 to 6, wherein the components of the active washing formulation(s) are selected from the group consisting of anionic, nonionic, cationic and
- 5 amphoteric surfactants, nonaqueous carriers, enzymes, dyes, fragrances, antibacterial agents, polymers, and rinse aids.

- 8. The composition portion as claimed in claim 6 or 7, wherein further components of the active washing formulation(s) are selected from the group consisting of solubilizers, UV stabilizers, defoamers, texturing 5 agents, corrosion inhibitors, preservatives, silver protectants, and additives gentle to the skin.
- 9. The composition portion as claimed in any of claims 1 to 8, wherein one active washing formulation is enclosed by a water-soluble polymer material 10 enclosure which forms a compartment.
- 10. The composition portion as claimed in any of claims 1 to 9, wherein at least two active washing formulations are enclosed by a water-soluble polymer material enclosure which forms at least two to compartments.
 - 11. The composition portion as claimed in claim 9 or 10, wherein said compartment(s) enclose(s) an amount of at least 1 ml of an active washing formulation.
- 12. A composition portion as claimed in any of 20 claims 1 to 11 for cleaning hard surfaces.
 - 13. A composition portion as claimed in any of claims 1 to 12 for cleaning hard surfaces by hand.
 - 14. A composition portion as claimed in any of claims 1 to 13 for dishwashing.